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(54) Process for the production of an oil-soluble nitrogen-containing lubricant additive and compositions containing them

(57) Oil-soluble nitrogen-containing dispersing agents suitable for use as lubricating oil additives are made by reacting a polyolefin-substituted succinic acid or anhydride with an amino compound having the formula:—

$NH_2.(CH_2)_2[NH.CH_2.CH(R).CH_2]_xNH_2$

or

$NH_2.[CH_2.CH(R).CH_2.NH]_y(CH_2)_2$
$[NH.CH_2CH(R).CH_2]_zNH_2$

in which formulae x, y and z are integers and R is either a hydrogen atom or a methyl radical. Amines used in Examples are
$NH_2(CH_2)_2NH(CH_2)_3NH_2$ and
$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

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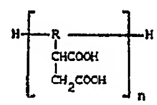
SPECIFICATION

Process for the production of an oil-soluble nitrogen-containing lubricant additive and compositions containing them

The present invention relates to oil-soluble nitrogen-containing products useful as additives in lubricating compositions. The products are particularly useful as dispersing agents in lubricating compositions intended for use in the crank case of an internal combustion engine.

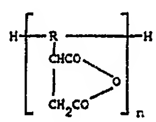
It has long been known that the internal combustion engine operating inefficiently forms large amounts of partial oxidation products, which enter the crank case of the engine by blowing past the piston rings. Most of these partial oxidation products are oil-insoluble, tending to form deposits on the various operating parts of the engine, such as the pistons, piston rings etc. It has therefore been the practice for the purpose of preventing the deposition of these products on the various engine parts to incorporate dispersants in the lubricating oil compositions, thus keeping the products highly dispersed in a condition unfavourable for deposition of metals. A class of compound which has found common acceptance as a dispersant additive is a polyolefin-substituted succinimide.

British Patent No. 922,831 describes a process for preparing an oil-soluble acylated amine suitable for use as a dispersant in lubricant compositions which comprises mixing a substituted succinic acid having the structural formula:



(I)

or a substituted succinic anhydride having the structural formula:



(II)

in which structural formula R is a large substantially aliphatic hydrocarbon radical having at least 50 carbon atoms and n is one or an integer greater than one, with at least one half of an equivalent amount of an amine of the formula:

$$H_2N(CH_2\underset{\displaystyle R^1}{\underset{|}{C}}HNH)_xH$$

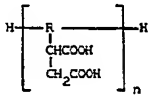
in which x is an integer and R^1 is a C_{1-6} alkyl radical or hydrogen, and heating the resulting mixture to effect acylation of the amine and remove the water formed in the reaction.

British Patent No. 1,021,183 describes and claims a product comprising an oil-soluble acylated nitrogen compound having within its structure (A) a substantially hydrocarbon substituted succinic radical which is a succinoyl, succinimidoyl, or succinoyloxy radical wherein the substantially hydrocarbon substituent contains at least 50 aliphatic carbon atoms and (B) a nitrogen-containing group having a nitrogen atom attached directly to the succinic radical (A), the remaining valence or valences of said nitrogen atom being satisfied by one or more hydrogen atoms or, as a substituent for a hydrogen atom, a hydrocarbon, hydroxyalkylamino-substituted hydrocarbon, hydroxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, amino, carbamyl, thiocarbamyl, guanyl, or acylimidoyl radical or an N-hydrocarbon-substituted amino, carbamyl, thiocarbamyl, guanyl or acylimidoyl radical.

Commercially available polyolefin succinimide dispersants are generally prepared by reacting a polyolefin substituted succinic acid or anhydride with an ethylene or polyethylene polyamine, otherwise known as ethylene amines. The ethylene amines are generally prepared by the reaction of ethylene dichloride with ammonia, which process results in the production of somewhat complex mixtures of ethylene amines, including cyclic condensation products such as piperazines. A desirable objective would be to prepare a dispersant additive from substantially pure amino compounds.

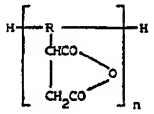
It has now been found that oil-soluble nitrogen-containing dispersing agents result when a polyolefin-substituted succinic acid or anhydride thereof is reacted with an amino compound of formula $NH_2.(CH_2)_2.[NH.CH_2.CH(R).CH_2]_xNH_2$ or $NH_2[CH_2.CH(R).CH_2NH]_yCH_2.CH_2.[NH.CH_2.CH(R).CH_2]_zNH_2$ wherein R is a hydrogen atom or a methyl group and x, y and z are integers in the range 1 to 10.

Thus according to the present invention there is provided a process for the production of an oil-soluble nitrogen-containing compound suitable for use as an additive in lubricating compositions which process comprises reacting a substituted succinic acid having the structural formula:



(I)

or a substituted succinic anhydride having the structural formula:



(II)

in which structural formulae (I) and (II) R is a substantially aliphatic hydrocarbon radical containing from 30 to 200 carbon atoms and n is one or an integer greater than one, with at least one-half an equivalent amount per equivalent of an amino compound or mixture of compounds having the formula:

$H_2N.(CH_2)_2[NH.CH_2.CH(R^1).CH_2]_xNH_2$ (III) or

$H_2N.[CH_2.CH(R^1).CH_2.NH]_y(CH_2)_2[NH.CH_2.CH(R^1).CH_2]_zNH_2$ (IV)

wherein in the formula (III) and (IV), R^1 is either a hydrogen atom or a methyl radical and x, y and z are integers in the range 1 to 10, the reaction between the compound of structural formula (I) or (II) and the amino compound of formula (III) or (IV) or mixture of such compounds being carried out under conditions which effect acylation of the amino compound or compounds.

Different types of compound may be formed during the acylation reaction. Thus amidation of the dicarboxylic acid or anhydride with the amino compounds of formula (I) or (II) can result in a simple acylic diamide, a cyclic diamide, a polymeric amide or a combination of any of these types of product. The amide groups may react further to form imide groups and, indeed, a substantial amount of this type of product may be formed. Other types of compound may also be formed.

Substituted succinic acids and anhydrides of structural formula (I) and (II) are well-known compounds in the art. Such compounds are readily made by the reaction of maleic anhydride with an olefin or a chlorinated olefin, the product being an alkenyl succinic anhydride. The reaction involves merely heating the two reactants at a temperature in the range 150 to 200°C. It will be appreciated that similar products can be prepared by an identical process in which a substantially aliphatic group such as an alkyl group is introduced as the substituent group. The substituent R is however, by preference, a polyolefin, preferably containing from 50 to 200 carbon atoms. Suitable polyolefins include polyethylene, polypropylene, polybutenes or mixtures of polybutenes etc. of which polyisobutene is preferred because of its availability and effectiveness in products deriving from it. Preferably n in the formulae (I) and (II) has the value one.

A suitable compound having the formula (III) is 3(2-amino ethylamino)propylamine i.e. $NH_2(CH_2)_2NH(CH_2)_3NH_2$ deriving from the substitution of R = a hydrogen atom and x = 1 in the formula (III). A suitable compound of formula (IV) is 1,2—01.(3-aminopropylamino)ethane i.e. $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ deriving from the substitution of R = a hydrogen atom and y and z = 1 in the formula (IV). Amino compounds of formula (III) in which x is equal to one may be prepared by the process comprising reacting ethylene diamine with either acrylonitrile or methacrylonitrile, preferably acrylonitrile, to produce an intermediate nitrile group-containing amino compound and thereafter hydrogenating the intermediate compound, suitably in the presence of a hydrogenation catalyst, thereby converting the nitrile group to an amino group. This sequence of steps may be repeated (x-1) times, each time increasing the chain length of the amino compound so produced by —$NH.CH_2.CH(R).CH_2$—. Thus the reaction may be represented by the following scheme:

$NH_2(CH_2)_2NH_2 + CH_2 = C(R).CN \rightarrow NH_2(CH_2)_2NH.CH_2.CH(R)CN$

$NH_2(CH_2)_2NH.CH_2.CH(R).CN \xrightarrow{H_2/Cat} NH_2(CH_2)_2.NH.CH_2.CH(R).CH_2NH_2$ and so on.

Amino compounds of formula (IV) may be prepared by increasing the proportion of the acrylonitrile or methacrylonitrile in the reaction mixture. This method of production provides amino compounds of greater purity than the ethylene dichloride/ammonia route. The compounds where R is a hydrogen atom are commercially available from Badische Anilin Und Soda Fabrik.

Although, at least one-half an equivalent amount of the amino compound of formula (III) or (IV) or mixture of such compounds must be reacted per mole equivalent of the substituted succinic acid of formula (I) or anhydride of formula (II), it is preferred to employ one equivalent per mole equivalent. Alternatively up to 2.0 chemical equivalents of the amino compound may be employed per mole equivalent of the acid or anhydride. The chemical equivalency of the amino compound of formula (III) or (IV) is based upon the nitrogen content of the compound i.e. one having four nitrogen atoms per molecule has a chemical equivalency of four equivalents per mole.

The acylation of the amino compound or mixture of compounds of formula (III) or (IV) with the substituted succinic acid of formula (I) or anhydride of formula (IV) is accompanied by the formation of water. It is very much preferred to remove the water formed in the reaction. Thus the reaction may be

carried out at a temperature in the range 80 to 200 preferably 100 to 200°C. A convenient method of carrying out the reaction is to incorporate an inert solvent such as a hydrocarbon solvent, of which toluene is preferred, in the reaction mixture and to remove the water formed in the reaction by azeotropic distillation.

According to another aspect of the present invention there is provided a lubricating oil composition which comprises a base oil of lubricating viscosity and an oil-soluble nitrogen-containing compound produced by the process as hereinbefore described.

The base oil of lubricating viscosity is preferably a crankcase lubricating oil.

In addition to the compound of the present invention the lubricating composition may also contain other additives conventionally employed in lubricant formulations, such as VI improvers, antioxidants, pour-point depressants, acid neutralisation agents, anti-wear agents etc.

The invention will now be illustrated by reference to the following Examples.

Preparation of bis-succinimide

EXAMPLE 1

505g (≡ 0.27 moles) polyisobutene succinic anhydride (PIBSA) of molecular weight 1870 was heated to 190°C and 15.8g $NH_2(CH_2)_2NH(CH_2)_3NH_2$ (≡ 0.135 moles) was added over a period of 15 minutes. Reaction was continued at 190°C for a period of 3 hours. Water formed by the reaction was removed under reduced pressure. The reaction product was then cooled.

The analysis of the product is given in Table 1.

EXAMPLE 2

Example 1 was repeated using 505g (≡ 0.27 mole) PIBSA and 23.5g $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

The analysis of the product is given in Table 1.

Preparation of mono-succinimides

EXAMPLE 3

Example 1 was repeated using 505g (≡ 0.27 mole) PIBSA and 28.5g (≡ 0.243 moles) $NH_2(CH_2)_2NH(CH_2)_3NH_2$.

The analysis of the product is given in Table 1.

EXAMPLE 4

Example 1 was repeated using 505g (≡ 0.27 moles) PIBSA and 42.4g $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

The analysis of the product is given in Table 1.

TABLE I

Product Analyses

Example No.	Product Type	Amino compound of formula (III) or (IV) used	N %	Basic N %	V210°F* cS	OPM 190B	OPM 308
1	Bis-	3-(2-amino ethylamino) propylamine	1.13	0.36	180	–	1A
2	Bis-	1,2-01(3-amino-propylamino) ethane)	1.42	0.66	181	–	1A
3	Mono-	3-(2-amino-ethylamino) propylamine	1.82	0.96	145	2	–
4	Mono-	1,2-01(3-amino-propylamino) ethane	2.4	1.56	147	2	–

*V210°F is the viscosity as measured at 210°F.

Engine Evaluation

EXAMPLE 5

The product of Example 1 was dissolved in a lubricant base oil to an alkalinity value of 25 mg KOH/g. The solutions were then evaluated in the Ring Belt Merit Test in a Petter AVI engine running under standard conditions.

The Ring Belt Merit (RBM) was derived from the average ratings of the four lands and three grooves on the piston. The scale runs from zero to ten, ten being the rating of maximum cleanliness.

The results of the RBM observations are given in Table 2.

EXAMPLE 6

The procedure of Example 5 was repeated except that the product of Example 2 was used in place of the product of Example 1.

The results of the RBM observations are given in Table 2.

EXAMPLE 7

The procedure of Example 5 was followed except that the product of Example 3 was used in place of the product of Example 1.

The results of the RBM observations are given in Table 2.

EXAMPLE 8

The procedure of Example 5 was followed except that the product of Example 4 was used in place of the product of Example 1.

The results of the RBM observations are given in Table 2.

TABLE 2

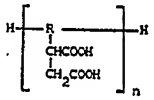
RBM Ratings

Example	Product Tested	RBM
5	Example 1	9.2
6	,, 2	8.8
7	,, 3	7.2
8	,, 4	3.9

The high values of the RBM for the bis-products of Examples 1 and 2 are indications of acceptable dispersancy properties.

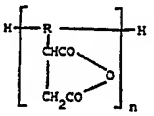
CLAIMS

1. A process for the production of an oil-soluble nitrogen-containing compound suitable for use as an additive in lubricating compositions which process comprises reacting a substituted succinic acid having the structural formula:



(I)

or a substituted succinic anhydride having the structural formula:



(II)

in which structural formulae (I) and (II) R is a substantially aliphatic hydrocarbon radical containing from 30 to 200 carbon atoms and n is one or an integer greater than one, with at least one-half an equivalent amount per equivalent of an amino compound or mixture of compounds having the formula:

$H_2N.(CH_2)_2/NH.CH_2.CH(R^1).CH_2/_xNH_2$ (III)

or $H_2N./CH_2.CH(R^1).CH_2NH/_y(CH_2)_2/NH.CH_2.CH(R^1).CH_2/_zNH_2$ (IV)

wherein in the formulae (III) and (IV), R^1 is either a hydrogen atom or a methyl radical and x, y and z are integers in the range 1 to 10, the reaction between the compound of structural formula (I) or (II) and the amino compound of formula (III) or (IV) or mixture of such compounds being carried out under conditions which effect acylation of the amino compound or compounds.

2. A process according to claim 1 wherein the substituent R in the substituted succinic acid of formula (I) and the substituted succinic anhydride of formula (II) is a polyolefin.

3. A process according to claim 2 wherein the polyolefin contains from 50 to 200 carbon atoms.

4. A process according to either one of claims 2 and 3 wherein the polyolefin is polyethylene, polypropylene or a polybutene or mixture of polybutenes.

5. A process according to any one of claims 2 to 4 wherein the polyolefin is polyisobutene.

6. A process according to any one of the previous claims wherein in the formulae (I) and (II) n has the value one.

7. A process according to any one of the previous claims wherein the compound of formula (III) is 3(2-aminoethylamino) propylamine.

8. A process according to any one of claims 1 to 6 wherein the compound of formula (IV) is 1,2—01.(3-aminopropylamino)ethane.

9. A process according to any one of the preceding claims wherein the amino compound of formula (III) in which x is equal to one is the compound prepared by the process comprising reacting ethylene diamine with either acrylonitrile or methacrylonitrile to produce an intermediate nitrile group-containing amino compound and thereafter hydrogenating the intermediate compound, thereby converting the nitrile group to an amino group.

10. A process according to claim 9 wherein ethylene diamine is reacted with acrylonitrile.

11. A process according to either one of claims 9 and 10 wherein the intermediate compound is hydrogenated in the presence of a hydrogenation catalyst.

12. A process according to any one of the preceding claims wherein the amino compound of formula (III) is the compound prepared by repeating (x-1) times the process claimed in any one of claims 8 to 10.

13. A process according to any one of the preceding claims wherein one equivalent of the amino compound of formulae (III) or (IV) or mixture of such compounds is reacted per mole equivalent of substituted succinic acid of formula (I) or substituted succinic anhydride of formula (II).

14. A process according to any one of claims 1 to 12 wherein up to 2.0 chemical equivalents of the amino compound of formula (III) or (IV) or mixture of such compounds are reacted per mole equivalent of the substituted succinic acid of formula (I) or substituted succinic anhydride of formula (II).

15. A process according to any of the previous claims wherein the reaction is carried out at a temperature in the range 80 to 200°C.

16. A process according to claim 15 wherein the temperature is in the range 100 to 200°C.

17. A process according to any one of the preceding claims wherein water formed in the reaction is removed.

18. A process according to any one of the preceding claims wherein a hydrocarbon solvent is incorporated in the reaction mixture and the water formed is removed by azeotropic distillation.

19. A process according to claim 18 wherein the hydrocarbon solvent is toluene.

20. A process for the production of an oil-soluble nitrogen-containing compound substantially as hereinbefore described with reference to the Examples.

21. Oil-soluble nitrogen-containing compounds whenever produced by a process as claimed in any one of the preceding claims.

22. A lubricating oil composition comprising a base oil of lubricating viscosity and an oil-soluble nitrogen-containing compound produced by the process as claimed in any one of claims 1 to 19.

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